

## PATENT SPECIFICATION

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7E2 9AC3R 22C29 22C8R 22C8T 22D3D1 22L1B 22L4D 22MX  
22N1A(72) Inventors JOHN THOMPSON and  
MICHAEL JAMES OWEN(54) ORGANOSILOXANE POLYAMIDE BLOCK  
COPOLYMERS

(71) We, DOW CORNING LIMITED formerly Midland Silicones Limited, a British Company of 12 Whitehall, London, SW1A 2DZ, formerly of Reading Bridge House, Reading, Berkshire, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to novel organosiloxane polyamide block copolymers and to a method for the preparation of such copolymers.

According to the invention there is provided an organosiloxane polyamide block copolymer comprising (1) at least one polyamide block comprising at least two units of the general formula



wherein R represents an alkylene radical having from 2 to 15 carbon atoms and (2) at least one organosiloxane block having at least two units of the general formula



wherein a has a value of 1, 2 or 3, R' represents a monovalent hydrocarbon radical, a monovalent halogenated hydrocarbon radical or a divalent radical of the formula —NR''X— wherein R'' represents a hydrogen atom, an alkyl radical, an aryl radical or a trihydrocarbonylsilyl radical in which not more than one of the hydrocarbon radicals has more than 5 carbon atoms and X represents a divalent organic radical attached to the nitrogen atom through a nitrogen-carbon linkage and to silicon through a silicon-carbon linkage,

wherein the free valency of the nitrogen atom is attached to a



group in a unit of a polyamide block as written above, there being at least one such group —NR''X— in the organosiloxane block.

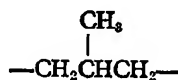
The block copolymers of this invention comprise at least one polyamide segment and at least one organosiloxane segment linked together through the divalent radical —NR''X—. The copolymers may be of several different types depending on the numbers and configurations of the constituent blocks. Thus, for example, they may have the configuration AB in which A represents the polyamide block and B the organosiloxane block or they may be of the type represented by ABA, BAB, (AB)<sub>x</sub> or BA<sub>y</sub> in which x and y are integers.

In the polyamide blocks the radical R may be any linear or branched radical having from 2 to 15 carbon atoms. Such blocks are derived from the polymerisation of a lactam, or the copolymerisation of two or more lactams e.g. caprolactam and lauryl-lactam, the preferred copolymers being those in which the polyamide blocks are derived from the commercially known lactams e.g. epsilon-caprolactam.

In the organosiloxane block each R' represents the specified divalent organic radical or a monovalent hydrocarbon or halogenated hydrocarbon radical, at least one R' being —NR''X—. The preferred monovalent R' substituents are those having less than 19 carbon atoms, for example alkyl radicals e.g. the methyl, ethyl, propyl, butyl, nonyl or octadecyl radicals, alkenyl radicals e.g. the vinyl, allyl or methallyl radicals, aryl radicals e.g. phenyl, naphthyl, benzyl or tolyl or haloalkyl radicals e.g. chloromethyl, trifluoropropyl

or bromophenyl, methyl radicals being preferred.

In the radical  $\text{—NR''X—}$  the symbol  $\text{R''}$  represents a hydrogen atom, an alkyl radical, e.g. methyl, ethyl, propyl, n-octyl, dodecyl or octadecyl radical, an aryl radical e.g. phenyl, benzyl or tolyl or a trihydrocarbonylsilyl radical in which not more than one of the hydrocarbon radicals has more than 5 carbon atoms. Examples of such radicals are trimethylsilyl, dimethylvinylsilyl, diethylphenylsilyl, dimethylphenylsilyl and n-octyldimethylsilyl. Preferably  $\text{R''}$  is hydrogen or an alkyl or aryl radical most preferably having less than 19 carbon atoms. The radical  $\text{X}$  may be any divalent organic radical which is linked at one end to a silicon atom of the organo-siloxane block through a silicon-carbon bond and at the other to the nitrogen atom by way of a carbon to nitrogen bond. Thus  $\text{X}$  may represent a divalent hydrocarbon radical, for example,



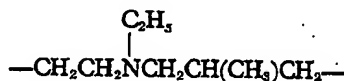
25 or the



radical, or a nitrogen containing hydrocarbon radical wherein the nitrogen atoms are present in  $\text{—C—N—C—}$  groups, for example the



radical or the



35 radical. The symbol  $\text{X}$  may also represent other organic radicals, for example radicals containing carbon, hydrogen and oxygen wherein the oxygen is present in the form of ether linkages or hydroxyl substituents e.g. the



40 and



radicals. The organic radical  $\text{X}$  may also consist of carbon, hydrogen and sulphur as in the



45 radical. The radical  $\text{X}$  may also be substituted with one or more polyamide blocks, for example as in



wherein  $\text{A}$  represents a polyamide block. Preferably  $\text{X}$  represents a divalent hydrocarbon radical. 50

The block copolymers of this invention may be prepared by a novel process involving effecting at least partial polymerisation of a lactam and reacting the polymerised or partially polymerised product with an organosiloxane having therein at least one silicon-bonded  $\text{NHR''X—}$  radical. 55

Included within the scope of this invention therefore is a process for the preparation of an organosiloxane-polyamide block copolymer the said process comprising (1) polymerising at least one lactam of the general formula 60



wherein  $\text{R}$  represents an alkylene radical having from 2 to 15 carbon atoms and (2) reacting the product of (1) with an organosiloxane having at least two units of the general formula 65



wherein  $\alpha$  has a value of 1, 2 or 3 and  $\text{R'''}$  represents a monovalent hydrocarbon radical, a monovalent halogenated hydrocarbon radical or a radical of the general formula  $\text{HNR''X—}$  wherein  $\text{R''}$  and  $\text{X}$  are hereinbefore defined, at least one  $\text{R'''}$  in the organosiloxane being the  $\text{HNR''X—}$  radical. 75

Examples of the lactams which may be employed to prepare block copolymers according to the process of this invention are propiolactam, pyrrolidone, capryl lactam, azacycloundecan-2-one and lauryl lactam, the preferred lactam being epsilon-caprolactam. If desired more than one lactam may be used to form the polyamide block or blocks in any given copolymer. 80

The organosiloxanes employed in the process of this invention are those having at least two units of the general formula



wherein  $\text{R'''}$  is a monovalent hydrocarbon radical or monovalent halogenated hydrocarbon radical as defined and exemplified herein in respect of  $\text{R'}$  or is the radical  $\text{HNR''X—}$  wherein  $\text{R''}$  and  $\text{X}$  are as hereinbefore defined. At least one  $\text{R'''}$  radical in the siloxane should be a  $\text{HNR''X—}$  radical. The organosiloxanes may vary from the disiloxanes up to the high molecular weight linear or branched polysiloxanes depending on the size of copolymer molecule desired and/or on the relative 100

weight of organosiloxane and polyamide segments in the copolymer. When the organosiloxane reactant is linear or substantially linear in configuration the groups  $\text{HNR}'\text{X}$ — may be present in terminal positions in the polymer molecule or disposed along the polymer chain. Methods of making the organosiloxane reactants are generally well-known in the art. For example, organosiloxanes in which the  $\text{HNR}'\text{X}$ — radical is an aminoalkyl radical may be prepared by the addition of a silylated allylamine e.g.  $(\text{CH}_3)_3\text{SiHNC}_2\text{H}_4\text{CH}=\text{CH}_2$  to a siloxane containing one or more  $\text{SiH}$  groups or by reaction of a silylated allylamine with a silane containing such groups and subsequent hydrolysis or cohydrolysis of the product. The silyl group may be retained or removed as desired. Organosiloxanes wherein X represents a group such as



may be prepared by the reaction of a chloropropyl-substituted alkoxy silane with ethylene diamine followed by hydrolysis or cohydrolysis of the reaction product.

Polymerisation of the lactam may be carried out in bulk or in organic solvent solution and at temperatures from above about  $80^\circ\text{C}$  to more than  $240^\circ\text{C}$ . In general the limiting factors with regard to the operative temperatures are the melting point of the lactam, the desired polymerisation rate and the thermal stability of the components of the reaction mixture. Most conveniently, the reaction is carried out at a temperature within the range from  $110$  to  $150^\circ\text{C}$ . Polymerisation of the lactam may be initiated and catalysed employing any of the initiators and catalysts known for this purpose, for example N-acetyl caprolactam. Preferably polymerisation is initiated by including in the reaction mixture an organic isocyanate or di-isocyanate e.g. phenyl isocyanate or phenyl di-isocyanate. The polymerisation is preferably catalysed by known means, for example with alkali or alkaline earth metals e.g. sodium, potassium lithium, calcium, strontium or compounds of such metals, for example hydrides, oxides, hydroxides and carbonates, the preferred catalysts being the metals and their hydrides. When the desired degree of polymerisation of the lactam to a polyamide is reached, the organosiloxane is introduced into the reaction mixture. The organosiloxane reacts with the polymerised lactam to form the organosiloxane polyamide block copolymer and terminates the polymerisation reaction.

The degree of polymerisation which the polyamide is permitted to attain will depend on the desired molecular weight of the polyamide segments of the block copolymer product. The configuration of the block copolymer will depend on the number and disposition of the  $\text{HR}'\text{NX}$ — radicals in the organosiloxane

reactant and also on the type of initiator employed for the polymerisation of the lactam. Thus for example, when the organosiloxane reactant contains only one of the specified functional radicals and the initiator is phenyl isocyanate the copolymer will have the AB configuration. When the organosiloxane contains one functional radical and phenyl di-isocyanate is used as initiator the copolymer will be of the BAB type, A representing the polyamide block. Similarly a difunctional organosiloxane used with phenyl isocyanate and phenyl di-isocyanate initiators will result in copolymers of the ABA and  $(\text{AB})_n$  types respectively.

It will of course be understood that when polymerisation of the lactam is carried out in the absence of a solvent the addition of the organosiloxane reactant should take place prior to the polymerised lactam attaining the molecular weight at which it solidifies at the polymerisation temperature. When the reaction is carried out in an organic solvent addition of the organosiloxane should take place prior to precipitation of the polyamide. The preferred solvents are the high boiling hydrocarbons e.g. deca-hydronaphthalene or amides free of active hydrogen atoms e.g. NN'-dimethylacetamide.

The block copolymers of this invention find application as additives for incorporation in polyamides to modify the processing and other properties thereof. Thus the ABA copolymers of this invention, when incorporated into nylon preferably in amounts of from 0.1 to 5 per cent by weight, provide the nylon polymer with a durable low energy surface having a low co-efficient of friction. Copolymers of the BAB type having suitable reactive terminal groups in the organosiloxane segments can be used to improve the bonding of nylon surfaces to glass. For such applications the preferred block copolymers are those in which the organosiloxane blocks have a molecular weight of from 150—15,000 and are composed predominantly of dimethylsiloxane units.

The following examples illustrate the invention.

#### Example 1

Dried and re-crystallised epsilon-caprolactam (10 g., 0.09 mole) was melted under argon at  $90^\circ\text{C}$ , a gas dispersion head being used to stir the melt. Phenyl isocyanate (0.32 g., 0.0026 mole) was injected into the melt and the temperature of the melt raised to  $120^\circ\text{C}$ . Sodium hydride (0.1 g., 0.002 mole) was then added as a dispersion in mineral oil, followed after 3 minutes by 2.2 g. (0.002 mole) of an  $\alpha,\omega$ -di-(aminopropyl)polydimethylsiloxane having a molecular weight of 1100. The reaction mixture was maintained at  $120^\circ\text{C}$  with stirring, for about two hours and then allowed to cool.

The product remaining was an ABA type

copolymer in which A represents a polyamide block and B a polydimethylsiloxane block. The copolymer was a white powdery solid which was insoluble in common organic sol-

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### Example 2

Dried and re-crystallised epsilon-caprolactam (11.3 g., 0.1 mole) was dissolved in deca-hydronaphthalene (45 ml.) and the solution heated to 120°C with stirring under an atmosphere of argon. Phenyl isocyanate (0.32 g., 0.0026 mole) was added to the solution followed by the sodium salt of epsilon-caprolactam (2.7 g., 0.002 mole) as catalyst. After 5 minutes the solution became cloudy and 1.6 g. (0.002 mole) of an  $\alpha,\omega$ -di-(aminopropyl)-polydimethylsiloxane (m.w.=800) added. The reaction was allowed to continue for 3 hours and the precipitated copolymer was isolated after this time by filtration. The product was an ABA type siloxane-polyamide copolymer, which was a white, insoluble powder.

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### Example 3

0.1 g., of the copolymer prepared in Example 1 was mixed thoroughly with 10 g., of commercial grade nylon 6. The mixture was pressed at 240°C into a disc of 2 inch diameter and 0.125 inch thickness using a 9 ton electrically heated press.

The critical surface tension of wetting ( $\sigma_c$ ) for the disc and for a control disc containing no block copolymer was obtained by measuring the contact angles of a series of methyl-alcohol/water mixtures placed on them. In order to check the permanence of the copolymer at the surface of the nylon, similar measurements were carried out on the copolymer-containing disc after refluxing in benzene for 16 hours. Measurements were also carried out on new surfaces prepared by removing a portion of the original surface of each disc with a scalpel. The results obtained were as follows:

	$\sigma_c$ (dynes $\text{cm}^{-1}$ )
Control disc	$29.5 \pm 0.5$
Disc containing copolymer	$19.5 \pm 0.5$
After reflux	$20.5 \pm 0.5$
Control (new surface)	$31.5 \pm 0.5$
Disc containing copolymer (new surface)	$23.0 \pm 0.5$

The above results show that the incorporation of the copolymer endowed the nylon with surface properties similar to those of a polydimethylsiloxane surface.

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### WHAT WE CLAIM IS:—

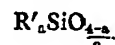
1. An organosiloxane-polyamide block copolymer comprising (1) at least one polyamide block comprising at least two units of the general formula

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wherein R represents an alkene radical having from 2 to 15 carbon atoms and (2) at least one organosiloxane block having at least two units of the general formula

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wherein a has a value of 1, 2 or 3, R' represents a monovalent hydrocarbon radical, a monovalent halogenated hydrocarbon radical or a divalent radical of the formula  $\text{—NR}''\text{X—}$  wherein R'' represents a hydrogen atom, an alkyl radical, an aryl radical or a trihydrocarbonylsilyl radical in which not more than one of the hydrocarbon radicals has more than 5 carbon atoms and X represents a divalent organic radical attached to the nitrogen atom through a nitrogen-carbon linkage and to silicon through a silicon-carbon linkage, wherein the free valency of the nitrogen atom is attached to a

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group in a unit of a polyamide block as written above there being at least one such group  $\text{—NR}''\text{X—}$  in the organosiloxane block.

2. A block copolymer as claimed in Claim 1 wherein R'' represents a hydrogen atom, an alkyl radical or an aryl radical.

3. A block copolymer as claimed in Claim 1 or Claim 2 wherein X represents a divalent hydrocarbon radical.

4. A block copolymer as claimed in any one of the preceding claims wherein the monovalent R' radicals are methyl radicals.

5. A process for the preparation of an organosiloxane-polyamide block copolymer which comprises (1) polymerising a lactam of the general formula

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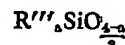
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wherein R represents an alkylene radical having from 2 to 15 carbon atoms and (2) reacting the product of (1) with an organosiloxane having at least two units of the general formula

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wherein a has a value of 1, 2 or 3 and R''' represents a monovalent hydrocarbon radical,

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- a monovalent halogenated hydrocarbon radical or a radical of the general formula  $\text{HNR}''\text{X}$ — wherein  $\text{R}''$  and  $\text{X}$  are as defined in Claim 1, at least one  $\text{R}'''$  in the organosiloxane being the  $\text{HNR}''\text{X}$ — radical.
- 5 6. A process as claimed in Claim 5 wherein  $\text{R}''$  represents a hydrogen atom, an alkyl radical or an aryl radical.
- 10 7. A process as claimed in Claim 5 or Claim 6 wherein (1) is epsilon-caprolactam.
8. A process as claimed in any one of Claims 5 to 7 wherein the lactam (1) is polymerised at a temperature within the range from 110 to 150°C.
- 15 9. A process as claimed in any one of Claims 5 to 8 wherein an organic isocyanate or di-isocyanate is employed as initiator for the polymerisation of the lactam.
10. A process as claimed in any one of Claims 5 to 9 wherein the polymerisation of the lactam (1) is carried out in the presence of an alkali or alkaline earth metal or hydride.
- 20 11. A process for the preparation of an organosiloxane-polyamide block copolymer substantially as described with reference to Example 1 or Example 2.
- 25 12. An organosiloxane-polyamide block copolymer whenever produced by the process claimed in any one of Claims 5 to 11 inclusive.

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